

# Screening of a macroion by multivalent ions: A new boundary condition for the Poisson-Boltzmann equation and charge inversion.

V. I. Perel<sup>1</sup> and B. I. Shklovskii

*Theoretical Physics Institute, University of Minnesota, 116 Church St. Southeast, Minneapolis, Minnesota 55455*

Screening of a macroion by multivalent counterions is considered. It is shown that ions form strongly correlated liquid at the macroion surface. Cohesive energy of this liquid leads to strong additional attraction of counterions to the surface. Away from the surface this attraction is taken into account by a new boundary condition for the Poisson-Boltzmann equation. This equation is solved with the new boundary condition for a charged flat surface and a long cylinder. For a cylinder Onsager-Manning theory loses its universality so that apparent charge of the cylinder is smaller than their theory predicts and depends on its bare charge. It can also vanish or change sign.

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## I. INTRODUCTION

Many polymers are strongly charged in a water solution. Lipid membranes, DNA and actin are the most famous examples of such biological polyelectrolytes. In a water solution polyelectrolytes are screened by smaller ions of both signs. Correct description of the screening of polyelectrolytes is tremendously important for calculation of properties of individual polyelectrolytes, for example, the effective charge or the bending rigidity. The screening also determines forces acting between polyelectrolytes and both thermodynamic and transport properties of their solutions. Here we concentrate on a rigid polyelectrolyte with a fixed charge distribution. Two standard problems are considered below – an infinite flat surface and an infinite cylinder – each uniformly charged with the surface density  $-\sigma < 0$ . The standard approach for a description of such problems is the Poisson-Boltzmann equation (PBE) for the selfconsistent electrostatic potential  $\psi(\mathbf{r})$

$$\nabla^2 \psi = -\frac{4\pi e}{D} \sum Z_i N_{0i} \exp\left(-\frac{Z_i e \psi}{k_B T}\right). \quad (1)$$

Here  $e$  is the charge of a proton,  $D \simeq 80$  is the dielectric constant of water,  $Z_i e$  is the charge of a small ion of sort  $i$  and  $N_{0i}$  is their concentration at the point where  $\psi = 0$ . The number of papers using the analytical and numerical solutions of Eq. (1) is extremely large<sup>2</sup>. On the other hand there is understanding that Eq. (1) neglects ion-ion correlations and is not exact. Deviations from the distribution of charge predicted by PBE were demonstrated numerically<sup>3,4</sup> for the following problem. Consider screening of a charged surface,  $x = 0$ , of a membrane or a film by a water solution occupying halfspace  $x > 0$ . Assume that there is only one sort of counterions with charge  $Ze > 0$  and their concentration  $N(x) \rightarrow 0$  at  $x \rightarrow \infty$ . In this case solution of Eq. (1) is very simple and has the Gouy-Chapman form

$$N(x) = \frac{1}{2\pi l} \frac{1}{(\lambda + x)^2}, \quad (2)$$

where  $\lambda = Ze/(2\pi l\sigma)$  is the Gouy-Chapman length,  $l = Z^2 l_B$  and  $l_B = e^2/(Dk_B T) \simeq 0.7$  nm is the Bjerrum length. At large  $Z$  and  $\sigma$ , the length  $\lambda$  can become of the order of the size of the water molecule or even smaller. For example, at  $Z = 3$  and  $\sigma = 1.0$  e/nm<sup>2</sup> length  $\lambda = 0.08$  nm. Thus, almost all counterions are located in the first molecular layer at the surface or, in other words, they condense at the very surface of polyelectrolyte. This raises question about a role of their lateral correlations and validity of Eq. (2). It was found by numerical methods<sup>4</sup> that for a typical charge density  $\sigma$  deviations from Eq. (2) are not large for monovalent counterions, but they strongly increase with the charge of counterions  $Z$ . It was suggested in Ref. 5, 6, 7, 8 that at  $Z \geq 2$  repulsion between multivalent counterions condensed at the surface is so strong that they form a two-dimensional strongly correlated liquid (SCL) in which the short order of counterions is similar to that of Wigner crystal (WC). This idea was used to demonstrate that two charged surfaces in the presence of multivalent counterions can attract each other at small distances.

The goal of this paper is to develop a simple analytical theory of the influence of SCL on a screening atmosphere of a single charged surface. It is shown below that the cohesive energy of SCL provides additional binding of ions to the surface. PBE fails to describe this correlation effect. At the same time, PBE works well far from the surface where  $N(x)$  is small and correlations are not important. To describe screening at large distances we derive a new boundary condition for  $N(x)$  at  $x = 0$ , which takes the effect of SCL into account. Then we solve PBE with this boundary condition for standard problems of screening of charged flat surface and a cylinder for different salt concentration  $N(\infty)$  in the bulk of solution. In the case of a cylinder, we show that in practical conditions the conventional picture of the Onsager-Manning<sup>9</sup> condensation should be strongly modified when dealing with multivalent ions. Since the counterions are tightly bound to the surface of cylinder the net linear charge density of a screened cylinder is smaller than in the Onsager-Manning theory and depends on a bare density. The net charge

density can also cross zero and become positive. In the case of a flat surface similar phenomena are found which lead to the screening atmosphere different from Eq. (2) and are in qualitative agreement with numerical results<sup>4</sup>. Because of simplicity and the use of the universal boundary condition our theory complements direct numerical methods<sup>4</sup> which until now were not able to study the case of  $Z \geq 3$  and other than planar geometries.

Let us present arguments for the existence of SCL and then derive a new boundary condition for  $N(x)$ . As we mentioned above and will show below for a typical  $\sigma \geq 1e \text{ nm}^{-2}$  and  $Z \geq 3$ , almost all charge of the plane is compensated by SCL of counterions at its surface, which has a two-dimensional concentration almost equal to  $n = \sigma/Ze$ . The minimum of Coulomb energy of counterion repulsion and their attraction to the background is provided by triangular close packed WC of counterions<sup>10</sup>. At  $T = 0$  the energy per ion of such WC,  $\varepsilon(n)$ , can be estimated as the energy of attraction,  $-Z^2e^2/DR$ , of an counterion to its Wigner-Seitz cell (correlation hole) which is approximately a disc with radius  $R = (\pi n)^{-1/2}$  and charge  $-Ze$ . More accurately

$$\varepsilon(n) = -\alpha n^{1/2} Z^2 e^2 D^{-1}, \quad (3)$$

where  $\alpha = 1.96$ . The inverse dimensionless temperature of SCL is usually written in units

$$\Gamma = \frac{Z^2 e^2}{RDk_B T} = 0.9 \frac{|\varepsilon(n)|}{k_B T}. \quad (4)$$

For example, at  $\sigma = 1.0 e/\text{nm}^2$  and room temperature, Eq. (4) gives  $\Gamma = 3.5, 6.4, 9.9$  at  $Z = 2, 3, 4$ . Thus for multivalent counterions we deal with low temperature situation.  $\Gamma$  is the large parameter of our theory. In its terms  $R/\lambda \simeq 2\Gamma \gg 1$  and  $l/R \simeq \Gamma \gg 1$ . For example, at  $Z = 3$  and  $\sigma = 1.0 e/\text{nm}^2$  lengths  $\lambda, R$  and  $l$  are equal to 0.08, 1.0, 6.3 nm respectively.

It is known<sup>11</sup>, however, that WC melts at very low temperature near  $\Gamma \simeq 130$ . So in the range of our interest,  $3 < \Gamma < 15$ , we deal with SCL. Thermodynamic properties of such SCL or one component plasma were studied numerically<sup>12,11</sup>. In the large range  $0.5 < \Gamma < 50$  excessive internal energy of SCL per counterion,  $\varepsilon(n, T) = k_B T f(\Gamma)$ , was fitted by the expression<sup>12</sup>

$$f(\Gamma) = -1.1\Gamma + 0.58\Gamma^{1/4} - 0.26 \quad (5)$$

with an error less than 2%. The first term on the right side of Eq. (5) dominates at large  $\Gamma$  and leads to Eq. (3). The other two terms provide a relatively small correction to the energy of WC. It is equal to 11% at  $\Gamma = 5$  and to 5% at  $\Gamma = 15$ . The reason for a such small difference is that short range order in SCL is similar to that of WC. For the free energy per unit area,  $F$ , we can write  $F = F(\Gamma = 0.5) + nk_B T \int_{0.5}^{\Gamma} f(\Gamma') d\Gamma'/\Gamma'$ , so that for the chemical potential which we need below to describe the equilibrium of SCL with the gas-like phase we obtain

$$\mu(n, T) = -k_B T \ln(n_w/n) + \mu_s + \mu_c(n, T), \quad (6)$$

$$\mu_c(n, T) = -k_B T (1.65\Gamma - 2.61\Gamma^{1/4} + 0.26 \ln \Gamma + 0.13). \quad (7)$$

Here  $\mu_c$  is contribution of correlations to the chemical potential and we replaced  $\mu(\Gamma = 0.5)$  by the chemical potential  $-k_B T \ln(n_w/n) + \mu_s$  of an ideal two-dimensional solution of ions in the surface layer of water with two-dimensional concentration  $n_w$ . The term  $\mu_s$  is the hydration free energy per ion at the surface and at  $n \ll n_w$  does not depend on the concentration of ions  $n$ . The first term of Eq. (7) corresponds to zero temperature WC and can be found directly from Eq. (3).

We show below that when an counterion moves away from SCL, it leaves behind its negatively charged correlation hole. We will also see that the potential energy of attraction to this hole becomes smaller than  $k_B T$  at  $x > l/4$ . On the other hand the selfconsistent potential of strongly screened surface is so small that it changes by  $k_B T$  only at exponentially large length  $\Lambda$ , which is defined below. Therefore the condition of equilibrium between SCL and the layer  $l/4 \ll x \ll \Lambda$  is

$$\mu(n) = \mu(N), \quad (8)$$

where  $\mu(n)$  is given by Eq. (6) and

$$\mu(N) = -k_B T \ln N_w/N + \mu_b \quad (9)$$

is the chemical potential of the bulk gas-like phase,  $N_w$  is the bulk concentration of water and  $\mu_b$  is the bulk hydration free energy which does not depend on  $N$ . Using Eq. (6) and Eq. (9) and solving Eq. (8) for  $N$  we obtain at  $l/4 \ll x \ll \Lambda$

$$N(0) = \frac{n}{w} \exp \left( -\frac{|\mu_c(n, T)|}{k_B T} \right), \quad (10)$$

where  $w = (n_w/N_w) \exp[(\mu_b - \mu_s)/k_B T]$ . Below we assume for simplicity that  $\mu_b = \mu_s$ . In this case  $w$  is the length of the order of size of the water molecule (for estimates we use  $w = 0.3 \text{ nm}$ ).

The notation  $N(0)$  reflects the fact that this value plays the role of a new boundary condition at  $x \ll \Lambda$  for solution of PBE which as we will see has large characteristic length  $\Lambda$ . Due to the large value of  $|\mu_c(n, T)|$ , the concentration  $N(0)$  can be very small. For example, at  $Z = 3$  and  $\sigma = 1.0 e/\text{nm}^2$ , when  $\Gamma = 6.4$  and according to Eq. (7)  $|\mu_c(n, T)|/k_B T = 7.0$  we obtain  $N(0) = 10^{24} \text{ m}^{-3} = 1.6 \text{ mM}$ . Switching to  $Z = 4$  we get  $\Gamma = 9.9$ ,  $|\mu_c(n, T)|/k_B T = 12.4$  and  $N(0) = 5.5 \text{ } \mu\text{M}$ . It is clear now that the  $|\mu_c(n, T)|$  plays in our problem the role similar to the work function for thermal emission or to the free energy of chemisorption. Thus we see that correlation effects in SCL provide nonspecific strong binding of counterions to the macroion surface. Qualitative arguments for such binding can be found in Ref. 4

We would like to stress that such binding does not happen at  $Z = 1$ . Indeed, at  $\sigma = 1.0 e/\text{nm}^2$  one

obtains from Eq. (4) and Eq. (7) that  $\Gamma = 1.2$  and  $\mu_c(n, T)/k_B T = 0.4$ . Therefore the boundary condition Eq. (10) does not produce nontrivial effects and standard solutions of PBE remain approximately valid.

Below we justify the role of the distance  $l/4$  and give an idea how  $N(x)$  evolves from  $n/\lambda$  at  $x \sim \lambda$  to  $N(0)$  at  $x = l/4$ . Let us move one ion of the crystal along the  $x$  axis. As we mentioned above, it leaves behind its correlation hole. In the range of distances  $\lambda \ll x \ll R$ , the correlation hole is approximately the disc of charge with radius  $R$  (the Wigner-Seitz cell) and the ion is attracted to the surface by its uniform electric field  $E = 2\pi\sigma/D$ . Therefore, if  $\lambda$  were larger than  $w$  we would get  $N(x) = (n/\lambda)\exp(-x/\lambda)$  at  $x \ll R$ . In the cases of our interest  $\lambda < w$  and  $N = n/w$  at  $x < w$ , while at  $w \ll x \ll R$

$$N(x) = \frac{n}{w} \exp(-x/\lambda). \quad (11)$$

At  $x \gg R$  the correlation hole radius grows and becomes of the order of  $x$ . Indeed SCL can be considered as a good conductor in the plane  $(y, z)$ . It is known that a charge at distance  $x$  from a metallic plane attracts an opposite charge into a disc with the radius  $\sim x$  or, in other words, creates its point like image on the other side of the plane at the distance  $2x$  from the original charge. The same thing happens to SCL. The removed ion repels other ions of SCL and creates a correlation hole in the form of the negative disc with the charge  $-Ze$  and the radius  $x$ . The correlation hole attracts the removed ion and decreases its potential energy by the Coulomb term  $U(x) = -Z^2 e^2 / 4Dx$ . This effect provides the correction to the activation energy of  $N(x)$ :

$$N(x) = \frac{n}{w} \exp\left(-\frac{|\mu(n)| - Z^2 e^2 / 4Dx}{k_B T}\right) \quad (x \gg R). \quad (12)$$

The similar “image” correction to the work function of a metal is well-known in the theory of thermal emission. The correction decreases with  $x$  and at  $x = l/4$ , becomes equal to  $k_B T$ , so that  $N(x)$  saturates at the value  $N(0)$ . The dramatic difference between the exponential decay of Eqs. (11), (12) and  $1/x^2$  law of Eq. (2) is obviously related to correlation effects neglected in PBE. Recall that it was assumed in the beginning of this paper that the charge of the surface is almost totally compensated by SCL. Exponential decay of  $N(x)$  with  $x$  confirms this assumption and at  $\Gamma \gg 1$  makes this theory self-consistent.

Consider now what happens with  $N(x)$  at distances  $x \gg l/4$ . At such distances, correlations of the removed ion with its correlation hole in SCL are not important and correlation between ions of the gas phase are even weaker because  $N(x)$  is exponentially small. Therefore, one can return to PBE. Solution of PBE with the boundary condition (10) and  $N(\infty) = 0$  is similar to Eq. (2):

$$N(x) = \frac{1}{2\pi l} \frac{1}{(\Lambda + x)^2} \quad (x \gg l/4), \quad (13)$$

where the new renormalized Gouy-Chapman length,  $\Lambda$ , is exponentially large

$$\Lambda = (2\pi l N(0))^{-1/2} = \sqrt{\frac{w}{2\pi n l}} \exp\left(\frac{|\mu_c(n, T)|}{2k_B T}\right). \quad (14)$$

For example, at  $\sigma = 1.0 \text{ e/nm}^{-2}$  Eq. (14) gives  $\Lambda \simeq 0.8, 5.3, 68 \text{ nm}$  at  $Z = 2, 3, 4$ . Comparing these lengths with  $l/4 = 0.7, 1.6, 2.8 \text{ nm}$  respectively we see that  $\Lambda \gg l/4$  for  $Z \geq 3$ , what justifies the use of Eq. (10) as the boundary condition for the large distance solution of PBE. At  $Z = 2$ , however,  $\Lambda \sim l/4$  and our theory works only qualitatively. This is the reason why we do not compare our  $N(x)$  quantitatively with numerical results<sup>4</sup>, obtained only for  $Z = 2$ .

Using Eq. (13) one finds that the total surface charge density located at distances  $x < l/4$

$$\sigma^* = -\sqrt{N(0)/(2\pi l_B)} = -\sigma(\lambda/\Lambda). \quad (15)$$

The exponentially small  $\sigma^*$  is a result of correlation effects, which strongly bind counterions to the surface. Corrections to  $\mu_c(n, T)$  and  $N(0)$  related to such small  $\sigma^*$  can be neglected. Until now we talked about the case when  $N(\infty) = 0$ . Let us now assume that there is a concentration  $N(\infty)$  of  $Z:1$  salt in the bulk of solution, so that in the bulk  $N(\infty)$  of counterions is neutralized by  $N_-(\infty) = ZN(\infty)$  of monovalent coions. This adds the Debye-Hückel screening radius

$$r_s = (4\pi l N(\infty)(1 + Z^{-2}))^{-1/2} \quad (16)$$

to the problem. If  $N(\infty) \ll N(0)$  screening radius  $r_s \gg \Lambda$  and the fact that  $N(\infty)$  is finite changes only the very tail of Eq. (13) making decay of  $N(x)$  at  $x \gg r_s$  exponential. At  $x \ll r_s$  still  $N(x) \gg ZN_-(x)$  and all previous results are valid. However, when  $N(\infty)$  approaches  $N(0)$ , the solution changes dramatically and  $\sigma^*$  vanishes. Indeed when  $N(\infty) = N(0)$  concentration  $N(x) = N(\infty)\exp(-Ze\psi/k_B T) = N(0)$  stays constant and potential  $\psi(x) = 0$  at  $x > l/4$ . This means that the surface is completely neutralized at distances  $0 < x < l/4$ .

If  $N(\infty) \gg N(0)$  negative charges dominate at  $x \ll r_s$ . Indeed in the PBE approach,  $N(x) = N(\infty)\exp(-Ze\psi/k_B T)$ ,  $N_-(x) = N_-(\infty)\exp(e\psi/k_B T)$  and when concentration  $N(x)$  decreases  $N_-(x)$  increases. One can derive a boundary condition for  $N_-(x)$  at  $x = 0$  from these equations

$$N_-(0) = ZN(\infty)[N(\infty)/N(0)]^{1/Z}, \quad (17)$$

where  $N(0)$  is given by Eq. (10). Then the solution of PBE for  $N_-(x)$  at  $x \ll r_s$  has the form similar to Eq. (13)  $N_-(x) = (2\pi l_B)^{-1}(\Lambda_- + x)^{-2}$ , where  $\Lambda_- = (2\pi l_B N_-(0))^{-1/2}$ . To compensate the bulk negative charge the positive surface charge density of SCL becomes larger than  $\sigma$ , so that the net surface charge density  $\sigma^* > 0$ . Similarly to Eq. (15), it is

$$\sigma^* = e \sqrt{N_-(0)2\pi l_B} = e/2\pi l_B \Lambda_- . \quad (18)$$

This phenomenon is called charge inversion and is, of course, impossible in the framework of the standard PBE. Technically, charge inversion follows from the small value of  $N(0)$  in Eq. (10). Its physics is related to the strong binding of counterions at the charged surface due to formation of SCL. Remarkably, when  $\Gamma \gg 1$ , this phenomenon happens under the influence of very small concentration of salt.

Let us switch to the screening of an infinite rigid cylinder with a radius  $a$ , a surface charge density  $-\sigma$  or, in other words, with a linear charge density  $\eta = -2\pi a\sigma$ . We assume that  $\sigma$  is large enough so that the surface of the cylinder is covered by a two-dimensional SCL with  $R < 2\pi a$  and with  $\Gamma \gg 1$ . (This means that the following important inequality,  $|\eta| \gg \eta_c = eZ/l$ , is satisfied). Such a cylinder can be a first order approximation for the double helix DNA, where  $a = 1$  nm,  $\eta = 5.9$  e/nm,  $\sigma = 0.94$  e/nm<sup>2</sup>, and at  $Z = 3$  length  $R \simeq 1$  nm and  $l = 6.3$  nm. Below we assume that, as in this example,  $l \gg a$ .

A screening atmosphere of a cylinder is described by concentration  $N(r)$ , where  $r$  is the distance from the cylinder axis. For  $|\eta| \gg \eta_c$  the solution of PBE is known<sup>13,2</sup> to confirm the main features of the Onsager-Manning<sup>9</sup> picture of the counterion condensation. The screening charge  $|\eta| - \eta_c$  is located at the cylinder surface, while the rest of the screening charge,  $\eta_c$ , at  $N(\infty) = 0$ , is spread in the bulk of the solution. This means that the net charge density of the cylinder,  $\eta^*$ , equals  $-\eta_c$  and does not depend on  $\eta$ . At a finite  $N(\infty)$  the charge density  $\eta^*$  is screened only at linear screening radius  $r_s$ .

Does SCL at the surface of the cylinder change these elegant statements? We show below that

$$\eta^* = -\eta_c \frac{\ln[N(0)/N(\infty)]}{\ln[4/(\pi N(\infty)l^3)]}. \quad (19)$$

It is clear from Eq. (19) that if two logarithms are close to each other, i. e. if  $\ln(N(0)^2 l^3 / N(\infty)) \gg 1$  the Onsager-Manning theory is approximately correct and  $\eta^*$  approaches  $-\eta_c$ . Note, however, that concentration  $N(0)$  itself is exponentially small so that values of  $N(\infty)$  at which  $\eta^*$  is close to  $-\eta_c$  are unrealistically small. On the other hand, in disagreement with the Onsager-Manning theory one obtains from Eq. (19) that  $|\eta^*| \ll \eta_c$  when concentration  $N(\infty)$  of the salt is still exponentially small, namely  $N(0)^2 l^3 \ll N(\infty) \ll N(0)$ . Moreover, according to Eq. (19)  $\eta^*$  vanishes at  $N(\infty) = N(0)$ . This result is easy to understand without calculations. Indeed, in this case  $N(r) = N(\infty) \exp(-Ze\psi(r)/k_B T) = N(0)$  stays constant and  $\psi(r) = 0$  at all  $r > l/4$ , so that all charge of the polyelectrolyte is compensated inside cylinder with  $r = l/4$ . The difference from the Onsager-Manning theory becomes even more apparent at  $N(\infty) > N(0)$  when the density  $\eta^*$  becomes positive, once more demonstrating the charge inversion. Note that the charge inversion takes place still at exponentially small  $N(\infty)$ . One can show that a positive  $\eta^*$  continues

to grow with growing  $N(\infty)$  until it reaches critical density  $e/l_B = \eta_c/Z$  at which Onsager-Manning condensation of monovalent coions begins. Charge  $\eta^*$  includes all counterions for which the binding energy exceeds  $k_B T$ . Therefore, anomalous charge density of a polyelectrolyte  $\eta^*$  can be measured in electrophoresis experiment. Finally, Eq. (19) shows that  $\eta^*$  does depend on bare charge density  $\eta$  through  $n$  in Eq. (10). Thus, for screening by multivalent ions at  $\Gamma \gg 1$  and at reasonably large  $N(\infty)$  all statements of Ref. 9, 13 are qualitatively incorrect.

To derive Eq. (19), we focus at distances  $l/4 < r < r_s$ , where the electrostatic potential of the linear charge density  $\eta^*$  is not screened and the boundary condition of Eq. (10) can be used to write

$$\begin{aligned} N(r) &= N(0) \exp\left(-\frac{Ze[\psi(r) - \psi(l/4)]}{k_B T}\right) \\ &\simeq N(0) \exp\left(\frac{2\eta_a}{\eta_c} \ln(4r/l)\right). \end{aligned} \quad (20)$$

At  $r = r_s$  concentration  $N(r_s) \simeq N(\infty)$ . Solving this equation for  $\eta^*$  we get

$$\eta^* = -\eta_c \frac{\ln[N(0)/N(\infty)]}{\ln(4r_s/l)^2}. \quad (21)$$

Finally, using Eq. (16), we arrive at Eq. (19)

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<sup>1</sup> Permanent address: A. F. Ioffe Physico-Technical Institute, 194021, St. Petersburg, Russia.

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